THE STRUCTURE OF THE PRODUCTS OF THE OPENING
OF THE PYRONE RING OF CHROMONES BY AMINES

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The fine structure of the products of the opening of the pyrone ring of chromones by amines — 2-(\(\beta\)-aminoacryloyl)phenols — has been determined.

The products of the cleavage of the pyrone ring of chromones by primary and secondary amines are usually ascribed the structure of \(\beta\)-aminovinyl ketones (I) (see [1-4]). The possible isomeric structure (A) has also been considered [5], since it was assumed that the pyrone ring is cleaved not by a molecule of amine but by a hydroxyl ion present in the water-containing reaction mixture. The production of identical substances by the reaction of amines with chromones and by the reaction of the same amines with the corresponding \(\beta\)-dicarbonyl compounds [5-7] is of little significance for a choice between the isomeric enamines mentioned, since the structure of the enamines synthesized by the second method has still been demonstrated insufficiently strictly. It is just for this reason that attempts were made — unfortunately unsuccessful [8] — to synthesize the enamine (Ia) from 1-\(\beta\)-diethylaminoacryloyl-2-methoxybenzene, the structure of which is known definitively.

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\begin{align*}
\text{Ia} & : R = H, R' = \text{C}_2\text{H}_5; & \text{Ib} & : R = H, \text{NR}_2 = \text{diperidine} \\
\text{II a} & : R = H, R' = \text{CH}_2\text{CH}_2; & \text{II b} & : R = \text{CH}_3\text{CH}_3
\end{align*}
\]

The choice between the structures I and A when \(R = H\) can be made without difficulty by means of the NMR spectra. Thus, in the NMR spectrum of compound Ib there is no signal of the proton of an aldehyde group, which should have appeared in the form of a doublet in the 9-10 ppm region, and at 5.83 ppm there is the doublet signal of \(H_\alpha\). The corresponding signal of \(H_\beta\) with \(\delta 7.83\) ppm falls partially in the region of the protons of the benzene ring. The narrow signal of the chelated hydroxyl has a chemical shift of 13.94 ppm. The spin-spin coupling constant of the \(H_\alpha\) and \(H_\beta\) vinyl protons is 12.2 Hz (in \(\text{D}_2\text{O}\)-DMSO solution, 15.5 Hz), which shows the trans configuration of Ib (with respect to the hydrogen atoms). In the IR spectrum of Ib (in \(\text{CHCl}_3\)) at 990 cm\(^{-1}\) there is a fairly strong band of the nonplanar deformation vibrations of the CH bonds of a trans CH = CH grouping. The fact that Ib belongs to the trans series has been reported previously [8].

The question of the fine structure of aminovinyl ketone I with primary and secondary amino groups and the possibility of prototropic tautomerism for these compounds has not hitherto been considered. It has been reported only that the phenolic hydroxyl forms an intramolecular hydrogen bond with the carbonyl...
We have studied the NMR spectra of compounds Ic, d. In the spectrum of Ic (Fig. 1, curve 1) at 5.77 ppm there is the doublet signal of $H_\alpha$ with $J$ 7.9 Hz (on the interpretation of the NMR spectra of $\beta$-aminovinyl carbonyl compounds see [11-14]). Consequently, the cis configuration (formula C) must be adopted for compound Ic. The multiplet signal of $H_\alpha$ is masked by the signals of the C$_2$H$_4$ protons. A fairly narrow signal with an intensity of 1 proton unit at $\delta$ 13.49 ppm must be ascribed to the proton of the phenolic OH group chelated with the carbonyl. The narrow signal at 9.3 ppm is due to the NH$_2$ proton, forming a hydrogen bond with the carbonyl. In the 5.1–5.9 ppm region there is a very broad signal with an area of approximately 1 proton unit of the NH$_2$ proton, which does not form a hydrogen bond; this signal is not sufficiently well identified, since it is overlapped by the doublet signal of $H_\alpha$.

The addition of CD$_3$OD to the solution causes the disappearance of all the signals of the OH and NH$_2$ groups. The IR spectrum of Ic in CCl$_4$ also agrees with this structure; in the 900–1010 cm$^{-1}$ region there are no trans-CH = CH bands. At 2400–3200 cm$^{-1}$ there are low-intensity diffuse bands of a chelated hydroxyl. The NH$_2$ group is characterized by stretching vibrations at 3515 cm$^{-1}$ (free NH$_2$) and at 3308 cm$^{-1}$ (bound NH$_2$; for the assignment of the bands in the IR spectra of $\beta$-aminovinyl ketones, see [15]). The intensity of the $\nu_{\text{NH}_2}$ bands and the values of their frequencies do not change on passing from a concentration of 0.01 to 0.002 M in CCl$_4$ solution. The saturation of such solutions with water has no effect on the appearance of these bands, but after a solution in CCl$_4$ has been shaken with deuterium oxide they disappear, and $\nu_{\text{ND}_2}$ vibrations appear at 2636 and 2435 cm$^{-1}$. At the same time it can be seen that the broad bands of a chelated OD group are located in the 2000–2400 cm$^{-1}$ region. The NMR spectrum of Id (Fig. 1, curve 2) has a doublet signal with $J$ 6.1 Hz at 4.48 ppm (determined at field frequencies of 100 and 60 MHz) with an intensity of 2 proton units caused by the protons of the benzyl CH$_2$ group, interacting with NH proton. A doublet with $J$ 7.7 Hz from $H_\alpha$ is located at 5.77 ppm. A broad signal at 10.21 ppm and a narrower signal at 13.78 ppm relate respectively, to NH and OH groups participating in the formation of hydrogen bonds with the carbonyl. Hence, it follows that Id exists in the form of the enamino ketone and not in the other possible tautomeric forms. In the IR spectrum of Id in CCl$_4$ solution at concentrations of 0.05 and 0.002 M, the bands of the stretching vibrations of a free NH group are absent, and there is a broad band of low intensity in the 3200–3300 cm$^{-1}$ region fusing with the broad band of the chelated hydroxyl at 2500–3200 cm$^{-1}$.

Thus, the products of the opening of the chromone ring by secondary amines contain a $\beta$-aminovinyl ketone fragment with the trans configuration (with respect to the hydrogen atoms of the vinyl group or the amino and CO groups), and the corresponding compounds with a primary or secondary amino group have the cis configuration stabilized by an intramolecular hydrogen bond between NH and CO groups, this bond being formed in spite of the fact that the carbonyl probably takes part simultaneously in the formation of a chelate hydrogen bond with the OH group. A similar phenomenon has been observed recently in the related compounds obtained by the reactions of amines with 1-(o-hydroxyphenyl)alkane-1,3-diones [16-17]. Other structures with intramolecular hydrogen bonds can be envisaged, but they are less probable, since they require a disturbance of the coplanarity of the systems of double conjugated bonds or the conversion of the benzene structure into a quinoid structure.

By analogy it may be considered that other compounds with a secondary amino group—for example, 2-(\(\beta\)-butylamino-\(\beta\)-n-butylaminocarbonylacryloyl)phenol (IIa) [4] and 3-(2-hydroxybenzylmethylene) piperazin-2-one (IIb) [3]—have the cis configuration with respect to the NH and CO groups. In the NMR spectrum of IIb in DMSO, the chemical shift of the signal of the vinyl proton is 6.75 ppm, and the signals of the protons of the C$_2$H$_4$ group are located in the 6.8–8.1 ppm region. The signals of the protons of the NH–C = O, NH–C = C, and OH groupings have chemical shifts of 8.69, 10.49 and 13.37 ppm. On the addition of CD$_3$OD to a solution of this substance in DMSO, the signal with $\delta$ 8.69 disappears most rapidly. The products